

UDC 48.33:548.4

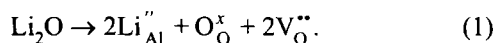
## STABILIZATION OF POLYMORPHIC PHASES IN OXIDES. OXYGEN VACANCIES

A. V. Belyakov<sup>1</sup>Translated from *Steklo i Keramika*, No. 3, pp. 19–22, March, 1999.

Polymorphic transitions in  $\text{Al}_2\text{O}_3$ , tungsten bronzes,  $2\text{CaO} \cdot \text{SiO}_2$ , and  $\text{ZrO}_2$  are considered. Considering that at high temperatures oxides usually have excess oxygen vacancies, a further increase in their concentration due to introduction of corresponding additives slows diffusion, impedes the polymorphic transition, and stabilizes the phase. Introduction of additives that result in an increased concentration of cation vacancies, on the other hand, accelerates diffusion and facilitates the polymorphic transition.

When a system is heated to high temperatures, the concentration of oxygen vacancies increases, and the system responds to this by a decrease in the cation vacancies in accordance with the Schottky equilibrium and thereby tries to restrain the rate of diffusion processes and, consequently, the probability of polymorphic transitions [1]. This probability can be increased by using additives that cause an increase in the concentration of cation vacancies through formation of solid solutions. Under these conditions these additives will accelerate the diffusional polymorphic transition.

In order to stabilize a low-temperature polymorphic oxide phase in heating, it is necessary to introduce additives that result in formation of oxygen vacancies. These additives increase further the concentration of oxygen vacancies. The system will be able to impede diffusion processes by a decrease in the concentration of cation vacancies. It is known that introduction of  $\text{Li}_2\text{O}$  into  $\gamma\text{-Al}_2\text{O}_3$  stabilizes this phase up to a temperature of  $1400^\circ\text{C}$ , whereas without additives this phase is usually stable up to  $800^\circ\text{C}$  [2]:



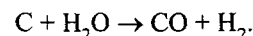
Oxygen vacancies stabilize a low-temperature phase.

In order to stabilize a polymorphic phase, it is necessary to increase the concentration of oxygen vacancies and decrease the concentration of cation vacancies. Moreover, additives that cause formation of anion vacancies should not result in formation of a liquid phase. The appearance of a liquid phase can shift the polymorphic-transition process to the liquid phase and thereby neutralize the effect of the concentration vacancies. The main problem of stabilization of a phase by an increase in oxygen vacancies is the fact that

many of the impurities that are necessarily present in the crystal cause the appearance of cation vacancies. This concentration depends on the impurity content and the type of solid solution (substitutional solution or interstitial solution). The impurities will accelerate the polymorphic transition and impede stabilization of the desired polymorphic phase.

The effect of vacancies on the transition  $\gamma \rightarrow \alpha$  in  $\text{Al}_2\text{O}_3$  is observed in introduction of additives of  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{La}_2\text{O}_3$  in the form of water-soluble salts in hydrolysis of aluminum sec-butoxide in transparent-ceramics technology. In heat treatment of aluminum hydroxide, some of the carbon of alkoxy groups remains in the powder. Additives of basic oxides ( $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{La}_2\text{O}_3$ ) facilitate binding of carboxide, which has an acid nature. The presence of carbon in an oxidized form is indicated by the fact that lengthy heat treatment in an oxidizing medium and even in oxygen did not result in its complete removal.

It was possible to remove all the carbon by passage of water vapor during heat treatment to a temperature of  $800^\circ\text{C}$  according to the reaction



The presence of  $\text{MgO}$ , which is the main additive by weight, caused stabilization of  $\gamma\text{-Al}_2\text{O}_3$  due to an excess in oxygen vacancies:

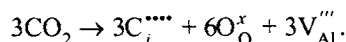


Protracted holding at a temperature of  $1100^\circ\text{C}$  did not result in conversion to  $\alpha\text{-Al}_2\text{O}_3$ . Samples molded from the powder obtained and fired in a vacuum furnace at a temperature of  $1800^\circ\text{C}$  were transparent but had substantial shrink-

<sup>1</sup> D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

age (over 30%) due to the polymorphic transition during sintering.

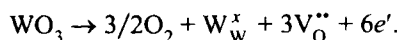
Retention of carbon drastically altered the results. At a temperature of 1100°C the powder converted completely to  $\alpha\text{-Al}_2\text{O}_3$ . The presence of  $\text{CO}_2$  in the solid solution produced aluminum vacancies:



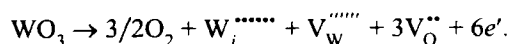
Aluminum vacancies increase the rate of diffusional mass transfer and of the polymorphic transition. Moreover, carbon together with additive aluminum cations and oxygen vacancies forms clusters and, possibly, nuclei of a new phase, which, in turn, can facilitate the appearance of  $\alpha\text{-Al}_2\text{O}_3$  nuclei.

It is more likely that  $\text{CO}_2$  is contained in the solid solution in the form of acid carbonates, for example,  $\text{MgCO}_3$ . However, acceleration of diffusion processes in sintering contributes to growth of crystals and capture of pores by them. Samples obtained from this powder were opaque, but their shrinkage was significantly lower, since no polymorphic transition occurred during sintering.

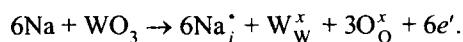
An excess of oxygen vacancies can account for the polymorphism of tungsten oxide and tungsten bronzes [3]. The high volatility of oxygen produces oxygen vacancies and free electrons  $e'$ :



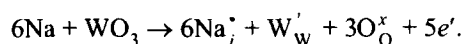
With a further increase in temperature, some of the tungsten cations pass to interstices with formation of tungsten vacancies, which creates conditions for diffusional transformations in the series of polymorphic modifications: triclinic, monoclinic, rhombic, and tetragonal:



Treatment of tungsten oxide in sodium vapor results in formation of tungsten bronze, whose temperatures of the corresponding transitions are significantly lower than in tungsten oxide. The higher the sodium concentration in the bronze, the lower the transition temperature, and with increasing temperature, a cubic modification appears after the tetragonal one. This can be accounted for by the fact that sodium, on entering the tungsten oxide lattice, binds the oxygen in the lattice, which prevents oxygen volatilization and the appearance of excessive oxygen vacancies:

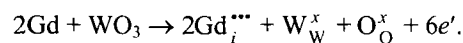


At the same time partial reduction of tungsten is possible:



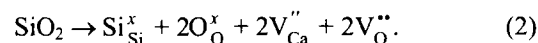
The use of elements whose degree of oxidation is higher than that of sodium but whose radius is similar (cadmium, gadolinium, thorium) results in the situation where the molar concentration of the additive is decreased in inverse propor-

tion to its degree of oxidation. For example, the amount of gadolinium required to produce the same concentration of defects is one-third the amount of sodium:

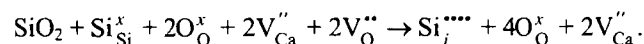


The high-temperature phase  $2\text{CaO} \cdot \text{SiO}_2$  is stabilized using various additives that form solid solutions. It is known that a solid solution of CaO in  $2\text{CaO} \cdot \text{SiO}_2$  results in stabilization of the high-temperature phase, and a solution of  $\text{SiO}_2$  in  $2\text{CaO} \cdot \text{SiO}_2$  destabilizes it [4]. Complex oxides deviate from stoichiometry not only toward a deficit of oxygen but also in the ratio of the cations they contain ( $\gamma$ -nonstoichiometry) [5]. Retardation of diffusional mass transfer will take place upon an increase not only in oxygen vacancies but also in vacancies of the fastest cation. At the same time, an increase in the concentration of vacancies of the slowest cation should accelerate mass transfer.

Synthesis of complex oxides from simple oxides usually produces a solid solution of the oxide containing the cation with a lower diffusion coefficient in the complex oxide and a phase that consists of the oxide containing the cation with a higher diffusion coefficient or is enriched in this oxide [6]. The solid-solution concentration depends on the degree of nonequilibrium of the process of synthesis. In formation of  $2\text{CaO} \cdot \text{SiO}_2$ , deviation from stoichiometry and the appearance of a solid solution of  $\text{SiO}_2$  in  $2\text{CaO} \cdot \text{SiO}_2$  are observed. At the same time, oxygen and calcium vacancies appear in  $2\text{CaO} \cdot \text{SiO}_2$ :

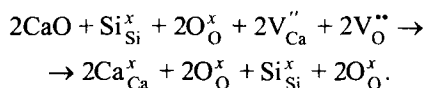


At first glance, a further increase in the  $\text{SiO}_2$  content in  $2\text{CaO} \cdot \text{SiO}_2$  will increase further the concentration of oxygen and calcium vacancies, which should retard the mass transfer. However, the concentration of oxygen vacancies in  $2\text{CaO} \cdot \text{SiO}_2$  is apparently close to the limit. As in the case with tungsten oxide described above, further addition of  $\text{SiO}_2$  (to the right part of Eq. (2)) increases the probability of  $\text{SiO}_2$  entering the interstices. At the same time, the concentration of oxygen vacancies becomes lower, and the probability of the polymorphic transition increases, i.e.,  $\text{SiO}_2$  acts as a destabilizer of the high-temperature form of  $2\text{CaO} \cdot \text{SiO}_2$ :



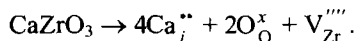
A decrease in the concentration of cation vacancies has a decisive effect.

Addition of CaO to the solid solution (to the right part of Eq. (2)) decreases the number of these vacancies and impedes the diffusional polymorphic transition:



The transition from the high-temperature cubic phase to the monoclinic phase in zirconium dioxide proceeds according to a diffusion mechanism, and the transition from the tetragonal to the monoclinic phase occurs without diffusion according to a martensite mechanism. The martensite transition requires only a slight shift of the ions and can occur very rapidly. The retardation of cracks in partially stabilized zirconium dioxide is based precisely on the possibility of the martensite transition proceeding at a speed equal to the speed of crack propagation [7]. However, oxygen vacancies and additives that form these vacancies have a decisive role in stabilization of the cubic and tetragonal phases. The martensite transition is usually preceded by diffusion processes that result in local redistribution of the stabilizing additive.

Zirconium dioxide is stabilized using oxides of alkali-earth metals, yttrium, scandium, and rare-earth elements. In replacing the zirconium cation all of them produce oxygen vacancies, which retards diffusional mass transfer and impedes the diffusional polymorphic transition to the low-temperature phase. Calcium and yttrium oxides are most widely used. It seems likely that calcium oxide partially dissolves in the form of  $\text{CaZrO}_3$ . Therefore, use of  $\text{CaZrO}_3$  instead of  $\text{CaO}$  facilitates formation of the high-temperature cubic phase and sintering due to the presence of zirconium vacancies [8]:



The dissolution in the form of calcium zirconate obviously facilitates entry of a calcium cation into an interstice in the form of a cluster. At high temperatures the cluster disintegrates, but a substantial part of the calcium cations remains in the interstices, which accelerates mass transfer. As the temperature decreases ( $1000^\circ\text{C}$ ), the clusters reappear. In this case not all calcium cations take part in formation of oxygen vacancies, which, consequently, decreases somewhat the oxygen electrical conductivity.

The magnesium cation has a somewhat smaller radius, and its electronegativity is closer to that of the zirconium cation, which facilitates its replacement. As concerns mass transfer, a part of the magnesium cations that is less than in the case of calcium oxide passes to the interstices in sintering. This is manifested in the higher anion conductivity of zirconium oxide stabilized by magnesium oxide, as compared to that stabilized by calcium oxide at a temperature above  $1500^\circ\text{C}$  [8]. However, with a decrease in temperature, a significantly greater part of the magnesium cations (as compared to calcium) is found at the zirconium lattice points. The increase in the vacancy concentration is limited by the stability of the crystallographic structure. The concentration of oxygen vacancies increases so much that the zirconium dioxide lattice loses its stability, and a martensite transition to

the tetragonal and monoclinic phases takes place. The oxygen vacancy concentration apparently decreases in this transition. This is similar to liquation. With high anion oversaturation, the system disintegrates into two locally stable ones, i.e., the development of an excessive amount of oxygen vacancies is open to the possibility of the system using another mechanism of developing dissipative structures, namely, division into two phases.

In the case of calcium oxide, the system, which is a solid, can redistribute the calcium cations between the lattice points and the interstices in accordance with the Le Chatelier-Brown principle so as to preserve the cubic phase. A similar situation arises in the system in the case of preservation of the spinel structure ( $\gamma$ -nonstoichiometry) [5]. As a result of partial evaporation of one of the oxides comprising the spinel, some cations of the other oxide pass over from octahedral vacancies formed by oxygen anions to tetrahedral vacancies. This enables the system to reduce the number of vacancies and preserve the spinel structure. The normal spinel transforms into partially converted spinel.

When magnesium oxide is used, such possibilities are significantly fewer, and therefore, the system comes to a bifurcation point, and spinoidal disintegration of the cubic phase begins.

The similar processes apparently occur in using yttrium and scandium oxides. Yttrium oxide forms the compound  $2\text{Y}_2\text{O}_3 \cdot 3\text{ZrO}_2$ , and scandium oxide does not form compounds with  $\text{ZrO}_2$ . The difference in the radii and the electronegativity as compared to the zirconium cation decreases from scandium to yttrium. Therefore, similarly to the comparison of the effect of calcium and magnesium additives, the oxygen electrical conductivity increases from yttrium to scandium [8].

Scandium replaces zirconium to a much greater extent than yttrium, instead of entering the interstices. The probability of cluster formation and entry of an yttrium cation into an interstice in cooling is significantly lower than for a calcium cation. Therefore, the oxygen electrical conductivity in using yttrium oxide is nearly twice that in using calcium oxide [8]. Compared to the calcium cation, the yttrium cation is closer in radius, electronegativity, and degree of oxidation to the zirconium cation. This makes solid solutions with yttrium oxide the most resistant to destabilization. Scandium oxide produces much more stable solid solutions compared to magnesium oxide and shows the highest oxygen electrical conductivity among known additives. The lanthanum cation has a larger radius and a greater difference in electronegativity with the zirconium cation than the yttrium cation. Lanthanum oxide and zirconium dioxide form the compound  $\text{La}_2\text{O}_3 \cdot \text{ZrO}_2$ . Therefore, solid solutions based on it are significantly less stable. They exist at temperatures above  $1800^\circ\text{C}$  [8].

Attempts to stabilize the monoclinic phase of  $\text{ZrO}_2$  by introducing additives were unsuccessful. The only exception was the introduction of  $\text{HfO}_2$ , which made it possible to in-

crease the transition temperature [9]. Apparently, in heating under ordinary conditions, the concentration of oxygen vacancies in  $\text{ZrO}_2$  is the highest possible, i.e., it is the saturation concentration. Attempts to increase this concentration further by introducing additives were unsuccessful and, accordingly, the monoclinic phase did not stabilize. The situation was different in introduction of  $\text{HfO}_2$ , which converts from the monoclinic to the tetragonal phase at a temperature of  $1900^\circ\text{C}$  [9] and forms a wide range of solid solutions with  $\text{ZrO}_2$ . As a consequence of the difference in ionic radii and resulting voltages, vacancies of both signs can appear, instead of prevailing oxygen vacancies [10]. With isovalent substitution and a wide range of solid solutions, the rule of additivity becomes valid, which results in an increased transition temperature.

To activate diffusional mass transfer, the vacancy ratio should approach the stoichiometric ratio of the ions in the basic material corrected for their mobility and motive force (Eq. (1)). If the amount and the parameters of the additive do not cause the system (namely, the sample) to deviate too far from dynamic equilibrium and at the same time retard the diffusion processes through an increased concentration of oxygen vacancies, the polymorphic transition is retarded, and the desired phase can be stabilized. Such additives act as stabilizers of the polymorphic phase. Otherwise, the system can pass to an unstable state, and the polymorphic transition will occur. The required cation vacancies can appear in replacement of the main-material cation by a cation with a higher degree of oxidation or in passage of some of the additive cations with any degree of oxidation to the interstices. Such additives act as destabilizers of the desired phase.

The concentration of oxygen vacancies cannot be above their solubility limit, and therefore the possibilities of stabilizing the desired phase are usually limited. An attempt to increase the concentration of oxygen vacancies by increasing the amount of the corresponding additive causes the additive cations to pass into the interstices, thus producing cation vacancies. Passage of an additive cation from a lattice point to an interstice is facilitated by its small radius and an increase in temperature, which increases the distance between the ions. As the temperature is decreased, preservation of the additive cation inside the interstice is facilitated by formation of clusters similar to chemical compounds that can be produced by the additive and the main phase. To achieve this, the electronegativity of the oxides of the additive and the main phase should differ significantly. However, an increased difference in electronegativity impedes formation of solid solutions and decreases the homogeneity region.

It is important to answer the question of whether the additive affects the height of the potential barrier that has to be

overcome for transition to a new phase (thermodynamics) or the probability of overcoming the barrier, which determines the transition velocity (kinetics). In the first case, the phase under should remain stable for an indefinitely long period the given conditions, and in the second case, long exposure necessarily causes the transition. This is, of course, an artificial contrast, since the thermodynamics and the kinetics are closely related. However, the predominant change in the height of the barrier is evidently observed when a wide range of solid solutions is formed upon isovalent substitution. In this case, the additivity rule comes into effect. For instance, addition of  $\text{HfO}_2$  to  $\text{ZrO}_2$  increases the temperature of the polymorphic transition from the monoclinic phase to the tetragonal phase, i.e., stabilizes the monoclinic phase of  $\text{ZrO}_2$  [9]. In the case of heterovalent substitution or formation of interstitial solid solutions, the solubility limit of the additive is usually low. In this case the barrier height evidently changes insignificantly, and it is basically the probability of overcoming the barrier that varies.

*The author acknowledges the assistance of Professor P. V. Kovtunenکو in useful discussion of the paper.*

## REFERENCES

1. A. V. Belyakov, "Stabilization of polymorphic phases in oxides. Polymorphic transitions," *Steklo Keram.*, No. 2, 16 – 17 (1999).
2. V. S. Gorshkov, V. G. Savel'ev, and N. F. Fedorov, *Physical Chemistry of Silicates and Other High-Melting Compounds* [in Russian], Vysshaya Shkola, Moscow (1988).
3. R. Collong, *Nonstoichiometry* [Russian translation], Mir, Moscow (1974).
4. H. Lehman, K. Niesel, and O. Thormann, "Die Stabilitätsbereiche der Modifikationen des Dicalciumsilikats," *Tonind.*, **93**(6), 197 – 209 (1969).
5. P. V. Kovtunenکو, "The effect of  $\gamma$ -nonstoichiometry on spinel inversion," *Steklo Keram.*, No. 8, 12 – 17 (1997).
6. A. V. Belyakov, "The effect of differences in the cation diffusion coefficients on deviation from stoichiometry in complex oxides," *Steklo Keram.*, No. 10, 18 – 20 (1997).
7. A. V. Belyakov and V. S. Bakunov, "Development of strong and crack-resistant structures in ceramics," *Steklo Keram.*, No. 1, 12 – 17 (1998).
8. D. S. Rutner, Yu. S. Toropov, S. Yu. Pliner, et al., *Highly Refractory Materials of Zirconium Dioxide* [in Russian], Metallurgiya, Moscow (1985).
9. S. K. Filatov, *High-Temperature Chemistry of Crystals. Theory, Methods, and Research Results* [in Russian], Nedra, Leningrad (1990).
10. A. V. Belyakov, E. S. Lukin, A. S. Vlasov, and V. P. Tarasovskii, "Certain principles of selection of additives for production of transparent ceramics," *Trudy MKhTI im. D. I. Mendeleeva*, Issue 117, 78 – 89 (1981).